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09 JUN 99 E453082-1 D02827
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3. Full name, address and postcode of the or of each applicant (underline all surnames)

PILKINGTON PLC
PRESCOT ROAD
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Patents ADP number (if you know it)

0444091001

66044 9001

If the applicant is a corporate body, give the country/state of its incorporation

ENGLAND

4. Title of the invention

IMPROVED PROCESS FOR COATING GLASS

5. Name of your agent (if you have one)

ANTHONY CHARLES HALLIWELL
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Country

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(if you know it)Date of filing
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Number of earlier application

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8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if:

YES

- a) any applicant named in part 3 is not an inventor, or
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Description 13

Claim(s) 4

Abstract 1

Drawing(s) 1 + 1

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Statement of inventorship and right to grant of a patent (Patents Form 7/77)

Request for preliminary examination and search (Patents Form 9/77)

1

Request for substantive examination (Patents Form 10/77)

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11. I/We request the grant of a patent on the basis of this application.

Signature *Anthony C. Halliwell*

Date 7 June 1999.

ANTHONY CHARLES HALLIWELL (AGENT FOR THE APPLICANT)

12. Name and daytime telephone number of person to contact in the United Kingdom

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Improved Process for Coating Glass

This invention relates to a process for the production of a photocatalytically active coated substrate, and in particular to a process for the production of a photocatalytically active coated glass.

It is known to deposit thin coatings having one or more layers, with a variety of properties on to substrates including glass substrates. One property of interest is photocatalytic activity which arises by the photogeneration, in a semiconductor, of a hole-electron pair when the semiconductor is illuminated by light of a particular frequency. The hole-electron pair can be generated in sunlight and can react in humid air to form hydroxy and peroxy radicals on the surface of the semiconductor. The radicals oxidise any organic grime on the surface. This property has an application in self-cleaning substrates, especially in self-cleaning glass for windows.

Titanium dioxide may be an efficient photocatalyst and may be deposited on substrates to form a transparent coating with photocatalytic self-cleaning properties. Titanium oxide photocatalytic coatings are disclosed in EP 0 901 991 A2, WO 97/07069, WO 97/10186 and WO 98/41480. In WO 98/06675 a chemical vapour deposition process is described for depositing titanium oxide coatings on hot flat glass at high deposition rate using a precursor gas mixture of titanium chloride and an organic compound as source of oxygen for formation of the titanium oxide coating. WO 98/06675 does not disclose the photocatalytic activity of any of the coatings produced using these processes.

Previously, it has been thought that relatively thick titanium oxide coatings need to be deposited to provide good photocatalytic activity. A problem of relatively thick titanium oxide coatings is high visible light reflection and thus relatively low visible light transmission.

The present invention aims to address the above mentioned problem.

The applicants have discovered that relatively thin titanium oxide coatings deposited using a mixture of titanium chloride and an ester have surprisingly high photocatalytic activity.

The present invention accordingly provides a process for the production of a photocatalytically active coated substrate which comprises depositing a titanium oxide coating having a thickness of less than 40 nm on a substrate by contacting a surface of the substrate with a fluid mixture comprising titanium chloride and an ester other than a methyl ester.

Preferably, the ester is an alkyl ester having an alkyl group with a β hydrogen (the alkyl group of an alkyl ester is the group derived from the alcohol in synthesis of an ester and a β hydrogen is a hydrogen bonded to the carbon atom β to the oxygen of the ether linkage in an ester). Preferably the ester is a carboxylate ester.

Suitable esters may be alkyl esters having a C₂ to C₁₀ alkyl group, but preferably the ester is an alkyl ester having a C₂ to C₄ alkyl group.

In a preferred embodiment of the invention the ester is a compound of formula:

R - C(O) - O - C(X)(X') - C(Y)(Y') - R', where R and R' represent hydrogen or an alkyl group, X, X', Y and Y' represent monovalent substituents, preferably alkyl groups or hydrogen atoms and wherein at least one of Y and Y' represents hydrogen.

Suitable esters that may be used in the process of the present invention include: ethyl formate, ethyl acetate, ethyl propionate, ethyl butyrate, n-propyl formate, n-propyl acetate, n-propyl propionate, n-propyl butyrate, isopropyl formate, isopropyl acetate, isopropyl propionate, isopropyl butyrate, n-butyl formate, n-butyl acetate and t-butyl acetate.

Preferably, the ester comprises an ethyl ester, more preferably the ester comprises ethyl formate, ethyl acetate or ethyl propionate. Most preferably the ester comprises ethyl acetate.

The present invention can be performed over a relatively wide temperature range of the substrate surface, but preferably is performed wherein the surface of the substrate is contacted with the fluid mixture when the substrate is at a temperature in the range 200°C to 750°C, more preferably in the range 400°C to 750°C, and most preferably in the range 600°C to 750°C.

The fluid mixture may be in the form of a liquid, especially dispersed as a fine spray (a process often referred to as spray deposition), but preferably the fluid mixture comprises a gaseous mixture. A deposition process performed using a gaseous mixture as precursor is often referred to as chemical vapour deposition (CVD). The preferred form of CVD is laminar flow CVD, although turbulent flow CVD may also be used.

In a preferred embodiment of the invention the substrate is substantially transparent and more preferably comprises a glass substrate. Preferably the glass substrate is a soda lime silica glass substrate.

Where the substrate is a soda lime glass substrate or other alkali metal ion containing substrate, the process of the present invention preferably additionally comprises depositing an alkali metal ion blocking layer on the surface of the substrate before depositing the titanium oxide coating. This is advantageous because alkali metal ions from the substrate may migrate into a coating deposited on the surface of the substrate which may reduce the photocatalytic activity of a coating deposited on the substrate.

The alkali metal ion blocking layer may comprise a metal oxide or silicon oxide. The alkali metal ion blocking layer may alternatively comprise silicon oxide containing carbon (often referred to as silicon oxycarbide and deposited as described in GB 2,199,848B) or silicon oxide containing nitrogen (often referred to as silicon oxynitride).

It is beneficial if the alkali metal ion blocking layer is thin enough to have no significant effect on the optical properties of the coating, especially by reducing the transparency of a transparent coated substrate or causing interference colours in reflection or transmission. The suitable thickness range will depend on the properties of the material used to form the alkali metal ion blocking layer (especially its refractive index), but usually the alkali metal ion blocking layer has a thickness of less than 60 nm and preferably has a thickness of less than 40 nm. Where present, the alkali metal ion blocking layer should always be thick enough to reduce or block migration of alkali metal ions from the glass into the titanium oxide layer.

The present invention may be performed on substrates of various dimensions including on sheet substrates, especially on cut sheets of glass, or preferably on-line during the float glass production process on a continuous ribbon of glass. Thus, preferably, the process is performed on-line during the float glass production process and the substrate comprises a glass ribbon. If the process is performed on line, it is preferably performed in the float bath.

An advantage of performing the invention on-line is that coatings deposited on-line tend to be durable and in particular to have good abrasion and chemical resistance.

An on-line deposition process is preferably, and other deposition processes may be, performed at substantially atmospheric pressure.

An advantage of the present invention is that the deposited titanium oxide layers are thin but the coated substrate produced by the invention still has excellent photocatalytic

activity. Preferably, the titanium oxide layer has a thickness of less than 30 nm, more preferably the titanium oxide layer has a thickness of less than 20 nm and most preferably the titanium oxide layer has a thickness in the range 2 nm to about 20 nm.

The present invention is also advantageous because depositing thin titanium oxide layers requires less precursor and the layers can be deposited in a relatively short time. A thin titanium oxide layer is also less likely to cause interference colours in reflection or transmission. However, a particular advantage is that the visible light reflection of a thin titanium oxide layer is low which is especially important when the coated substrate is coated glass. Preferably, the process is such that a coated glass produced by the process has a visible reflection measured on the coated side of less than 35%, more preferably of less than 20% and most preferably of less than 17%. This is advantageous because low light reflection corresponds to high visible transmission which is often required in architectural and especially automotive applications of glass.

Usually the required visible light transmission of the coated glass to be produced by the process of the invention will determine the thickness of the titanium oxide layer.

Preferably, the process is such that the coated substrate produced by the process has a haze of less than 1%, which is beneficial because this indicates good clarity of view through a transparent coated substrate.

Preferably, the process of the present invention is such that a coated glass produced by the process has a static water contact angle on the coated face of less than 20°. The static water contact angle is the angle subtended by the meniscus of a water droplet on a glass surface and may be determined by measuring the diameter of a water droplet of known volume on a glass surface and calculated using an iterative procedure. A static water contact angle of lower than about 40° indicates a hydrophilic surface.

Photocatalytic activity may be determined by measuring the rate of decrease of the integrated absorbance of the infra-red absorption peaks corresponding to the C-H stretches of a thin film of stearic acid, formed on the coated substrate, under illumination by UV light. Coated substrates produced by the process of the present invention will usually have a photocatalytic activity (when illuminated by a UVA lamp having an intensity of about 32 W/m² and a peak wavelength of 351 nm), of greater than 4 x 10⁻²cm⁻¹min⁻¹, preferably greater than 6 x 10⁻²cm⁻¹min⁻¹ and more preferably greater than 8 x 10⁻²cm⁻¹min⁻¹.

Thus in a further aspect, the present invention provides a coated glass comprising a glass substrate having a photocatalytically active titanium oxide coating on one surface thereof, characterised in that the coated surface of the glass has a photocatalytic activity of greater than $8 \times 10^{-2} \text{ cm}^{-1} \text{ min}^{-1}$ and in that the coated glass has a visible light reflection measured on the coated side of less than 20%

Coated substrates produced by the process of the present invention have uses in many areas including in a multiple glazing unit comprising a first glazing pane of a coated substrate in spaced opposed relationship to a second glazing pane, or, when the coated substrate is coated glass, as laminated glass comprising a first glass ply of the coated glass, a polymer interlayer (of, for example, polyvinylbutyral) and a second glass ply.

The invention is illustrated but not limited by the following drawing.

The Figure is a graph of photocatalytic activity of coated glass produced by a process according to the invention as a function of the thickness of the titanium oxide layer.

In the Figure the coated glasses were produced using an on-line CVD process as described in the Examples, below. The open circles 1 relate to titanium oxide layers deposited by a process according to the invention. The crosses 2 relate to titanium oxide layers deposited using titanium ethoxide as titanium precursor and are comparative.

The invention is further illustrated by the following Examples, in which coatings were applied by laminar flow chemical vapour deposition in the float bath on to a moving ribbon of float glass during the glass production process. In the Examples two layer coatings were applied to the glass ribbon.

All gas volumes are measured at standard temperature and pressure unless otherwise stated. The thickness values quoted for the layers were determined using high resolution scanning electron microscopy and optical modelling of the reflection and transmission spectra of the coated glass. Thickness of the coatings was measured with an uncertainty of about 5%. The transmission and reflection properties of the coated glasses were determined using an Hitachi UV 4000 spectrophotometer (illuminant D65). The L* values mentioned herein of the transmission colour of the glasses refer to the CIE Lab colours. The haze of the coated glasses was measured using a Hazeguard haze meter.

The photocatalytic activity of the coated glasses was determined from the rate of decrease of the area of the infrared peaks corresponding to C-H stretches of a stearic acid

film on the coated surface of the glass under illumination by UVA light. The stearic acid film was formed on samples of the glasses, 7-8 cm square, by spin casting 20 μ l of a solution of stearic acid in methanol (8.8×10^{-3} mol dm $^{-3}$) on the coated surface of the glass at 2000 rpm for 1 minute. Infra red spectra were measured in transmission, and the peak height of the peak corresponding to the C-H stretches (at about 2700 to 3000 cm $^{-1}$) of the stearic acid film was measured and the corresponding peak area determined from a calibration curve. The coated side of the glass was illuminated with a UVA-351 lamp (obtained from the Q-Panel Co., Cleveland, Ohio, USA) having a peak wavelength of 351 nm and an intensity at the surface of the coated glass of approximately 32 W / m 2 .

The static water contact angle of the coated glasses after irradiation using the UVA 351 lamp for about 2 hours was determined by measuring the diameter of a water droplet (volume in the range 1 to 5 μ l) on the surface of the coated glass.

Examples 1-15

A ribbon of 1 mm thick soda lime float glass advancing at a lehr speed of 300 m/hour was coated with a two-layer coating as the ribbon advanced over the float bath at a position where the glass temperature was in the range of about 650°C to about 670°C. The float bath atmosphere comprised a flowing gaseous mixture of nitrogen and 9% hydrogen at a bath pressure of approximately 0.15 mbar.

Layer 1 (the first layer to be deposited on the glass) was a layer of silicon oxide (silica). Layer 1 was deposited by causing a gaseous mixture of monosilane (SiH₄, 60 ml/min), oxygen (120 ml/min), ethylene (360 ml/min) and nitrogen (8 litres/min) to contact and flow parallel to the glass surface in the direction of movement of the glass using coating apparatus as described in GB patent specification 1 507 966 (referring in particular to Fig. 2 and the corresponding description on page 3 line 73 to page 4 line 75) with a path of travel of the gaseous mixture over the glass surface of approximately 0.15 m. Extraction was at approximately 0.9 to 1.2 mbar. The glass ribbon was coated across a width of approximately 10 cm at a point where its temperature was approximately 670°C. The thickness of the silica layer was about 20 to 25 nm.

Layer 2 (the second layer to be deposited) was a layer of titanium dioxide. Layer 2 was deposited by delivering (through lines maintained at about 250 °C) a gaseous mixture

comprising titanium tetrachloride in flowing nitrogen carrier gas and ethyl acetate in flowing nitrogen carrier gas and a bulk flow of nitrogen of 8 l / min (flow rate measured at 20 psi) to coating apparatus consisting of an oil cooled dual flow coater. The pressure of the nitrogen carrier and bulk nitrogen gases was approximately 20 pounds per square inch. The gaseous mixture contacted and flowed parallel to the glass surface both upstream and downstream along the glass ribbon. The path of travel of the gaseous mixture downstream was about 0.15 m and upstream was about 0.15 m. Extraction in the direction downstream was about 1.4 mbar and upstream was about 1.6 mbar. Titanium tetrachloride and ethyl acetate were entrained in flowing nitrogen carrier gas by passing nitrogen through bubblers containing either titanium tetrachloride or ethyl acetate. The flow rates of the nitrogen carrier gas are described in Table 1 (the flow rates were measured at 20 psi). The titanium tetrachloride bubbler was maintained at a temperature of 69°C and the ethyl acetate bubbler was maintained at a temperature of 42°C. The estimated flow rates of entrained titanium tetrachloride and entrained ethyl acetate are also described in Table 1 for each of the Examples 1 to 15.

The properties of the two-layer coatings were measured. Values of the thickness of layer 2 (the titanium oxide layer), and values of the visible reflection measured on the coated side and L* of the coated glasses are described in Table 2 for the Examples 1-15. The haze of each coated glass was below 0.2 %.

The photocatalytic activity and static water contact angle of the coated glasses were determined. The initial peak height and initial peak area of the IR peaks corresponding to the stearic acid C-H stretches, the photocatalytic activity and the static water contact angle for each of the Examples 1-15 are described in Table 3.

Comparative Examples A-J

The Comparative Examples were conducted under the same conditions as Examples 1-15 except that layer 2 was deposited from a gaseous mixture comprising titanium tetraethoxide entrained in nitrogen carrier gas by passing the carrier gas through a bubbler containing titanium tetraethoxide maintained at a temperature of 170°C (Comparative Examples A-H) or 168°C (Comparative Examples I to J) and except that the bath pressure for Comparative Examples I and J was 0.11 mbar. The flow rates of nitrogen carrier gas (measured at 20 psi) and titanium tetraethoxide were as described in

Table 4 for each of the Comparative Examples A-J. The flow rate of bulk nitrogen gas was 8.5 l/min (measured at 20 psi).

The properties of the two-layer coatings were measured. Values of the thickness of layer 2 (the titanium oxide layer), and values of the visible reflection measured on the coated side of the coated glasses are described in Table 5 for the Comparative Examples A-J. The haze of each coated glass was below 0.7%.

The photocatalytic activity and static water contact angle of the coated glasses were determined. The initial peak height and initial peak area of the IR peaks corresponding to the stearic acid C-H stretches, the photocatalytic activity and the static water contact angle for each of the Comparative Examples A-J are described in Table 6.

TABLE I

| Example | Nitrogen Carrier Gas Flow Rates to Bubblers (l / min, measured at 20 psi) | | TiCl ₄ flow rate (l / min) | Ethyl Acetate flow rate (l / min) |
|---------|---|-----------------------|---------------------------------------|-----------------------------------|
| | TiCl ₄ Bubbler | Ethyl Acetate Bubbler | | |
| 1 | 0.16 | 1 | 0.032 | 0.46 |
| 2 | 0.12 | 0.3 | 0.024 | 0.14 |
| 3 | 0.12 | 0.45 | 0.024 | 0.21 |
| 4 | 0.08 | 0.2 | 0.016 | 0.09 |
| 5 | 0.12 | 0.15 | 0.024 | 0.07 |
| 6 | 0.12 | 0.75 | 0.024 | 0.35 |
| 7 | 0.08 | 0.3 | 0.016 | 0.14 |
| 8 | 0.08 | 0.5 | 0.016 | 0.23 |
| 9 | 0.04 | 0.1 | 0.008 | 0.05 |
| 10 | 0.04 | 0.15 | 0.008 | 0.07 |
| 11 | 0.04 | 0.25 | 0.008 | 0.12 |
| 12 | 0.16 | 0.1 | 0.032 | 0.05 |
| 13 | 0.08 | 0.1 | 0.016 | 0.05 |
| 14 | 0.16 | 0.4 | 0.032 | 0.19 |
| 15 | 0.16 | 0.2 | 0.032 | 0.09 |

TABLE 2

| Example | Thickness of titanium oxide layer (nm) | Visible reflection of coated glass (%) | L* value of coated glass (%) |
|---------|--|--|------------------------------|
| 1 | 15 | 14.1 | 44 |
| 2 | 14.3 | 13.9 | 44 |
| 3 | 14.2 | 13.2 | 43 |
| 4 | 11.3 | 11.4 | 40 |
| 5 | 12.1 | 12.1 | 41 |
| 6 | 11.0 | a | a |
| 7 | 8 | a | a |
| 8 | 7.2 | 9.7 | 37 |
| 9 | 6.1 | 9.1 | 36 |
| 10 | 5.6 | 9 | 36 |
| 11 | 4.6 | 8.7 | 35 |
| 12 | 15.6 | 15.4 | 46 |
| 13 | 16.0 | a | a |
| 14 | 17.5 | 16.2 | 47 |
| 15 | 20.3 | 19.5 | 51 |

a Not measured

TABLE 3

| Example | IR Peaks corresponding to stearic acid film C-H stretches (2700 – 3000 cm^{-1}) | | Photocatalytic Activity ($\times 10^{-2}$ $\text{cm}^{-1} \text{ min}^{-1}$) | Static Water Contact Angle ($^{\circ}$) |
|---------|---|---|--|---|
| | Initial Peak Height (arbitrary units) | Initial Peak Area (cm^{-1}) | | |
| 1 | 0.030 | 1.04 | 9.4 | 17 ± 5 |
| 2 | 0.0331 | 1.15 | 10.4 | 15 ± 1 |
| 3 | 0.0311 | 1.08 | 12.2 | 13 ± 2 |
| 4 | 0.0324 | 1.13 | 6.8 | 14 ± 1 |
| 5 | 0.0287 | 1.00 | 8.2 | 16 ± 3 |
| 6 | 0.028 | 0.98 | 8.8 | 15 ± 1 |
| 7 | 0.0343 | 1.20 | 10.8 | 15 ± 1 |
| 8 | 0.0289 | 1.03 | 6.6 | 16 ± 1 |
| 9 | 0.0289 | 1.01 | 6.5 | 14 ± 2 |
| 10 | 0.0278 | 0.97 | 6.2 | 18 ± 2 |
| 11 | 0.0344 | 1.20 | 5.4 | 18 ± 1 |
| 12 | 0.0291 | 1.02 | 10.2 | 12 ± 1 |
| 13 | 0.0289 | 1.01 | 9.1 | 14 ± 2 |
| 14 | 0.0269 | 0.94 | 9.4 | 15 ± 2 |
| 15 | 0.0331 | 1.15 | 8.7 | 15 ± 2 |

TABLE 4

| Comparative Example | Nitrogen Carrier Gas Flow Rates to Titanium tetraethoxide bubbler (l / min, measured at 20 psi) | Titanium ethoxide flow rate (l / min) |
|---------------------|---|---------------------------------------|
| A | 0.25 | 0.014 |
| B | 0.15 | 0.008 |
| C | 0.2 | 0.011 |
| D | 0.25 | 0.014 |
| E | 0.3 | 0.017 |
| F | 0.35 | 0.019 |
| G | 0.2 | 0.011 |
| H | 0.1 | 0.006 |
| I | 0.6 | 0.030 |
| J | 0.4 | 0.020 |

TABLE 5

| Comparative Example | Thickness of titanium oxide layer (nm) | Visible reflection of coated glass (%) |
|---------------------|--|--|
| A | 13 | a |
| B | 13 | a |
| C | 16 | 15.7 |
| D | 18 | a |
| E | 24 | a |
| F | 26 | a |
| G | 9.9 | 10.9 |
| H | 4.7 | 8.8 |
| I | 38.3 | 35.2 |
| J | 31.9 | 28.4 |

a Not measured

TABLE 6

| Comparative Example | IR Peaks corresponding to stearic acid film C-H stretches (2700 – 3000 cm ⁻¹) | | Photocatalytic Activity (x 10 ⁻² cm ⁻¹ min ⁻¹) | Static Water Contact Angle (°) |
|---------------------|---|---------------------------------------|--|--------------------------------|
| | Initial Peak Height (arbitrary units) | Initial Peak Area (cm ⁻¹) | | |
| A | 0.027 | 0.953 | 5.7 | 19±5 |
| B | 0.031 | 1.095 | 5.7 | ^a |
| C | 0.024 | 0.838 | 3.6 | 15±2 |
| D | 0.030 | 1.029 | 7.1 | 11±3 |
| E | 0.029 | 1.015 | 7 | 17±3 |
| F | 0.031 | 1.071 | 7.4 | 13±4 |
| G | 0.031 | 1.085 | 4.4 | 21±3 |
| H | 0.029 | 0.998 | 3.2 | 16±5 |
| I | 0.021 | 0.733 | 3.6 | 13 |
| J | 0.024 | 0.848 | 3.3 | 14 |

a Not measured

CLAIMS

1. A process for the production of a photocatalytically active coated substrate which comprises depositing a titanium oxide coating having a thickness of less than 40 nm on a substrate by contacting a surface of the substrate with a fluid mixture comprising titanium chloride and an ester other than a methyl ester.
2. A process as claimed in claim 1 wherein the ester is an alkyl ester having an alkyl group with a β hydrogen.
3. A process as claimed in claim 1 or claim 2 wherein the ester is a carboxylate ester.
4. A process as claimed in any one of the preceding claims wherein the ester is an alkyl ester having a C₂ to C₄ alkyl group.
5. A process as claimed in any one of the preceding claims wherein the ester is a compound of formula: R - C(O) - O - C(X)(X') - C(Y)(Y') - R', where R and R' represent hydrogen or an alkyl group, X, X', Y and Y' represent monovalent substituents and wherein at least one of Y and Y' represents hydrogen.
6. A process as claimed in any one of the preceding claims wherein the ester comprises ethyl formate, ethyl acetate, ethyl propionate, ethyl butyrate, n-propyl formate, n-propyl acetate, n-propyl propionate, n-propyl butyrate, isopropyl formate, isopropyl acetate, isopropyl propionate, isopropyl butyrate, n-butyl formate, n-butyl acetate or t-butyl acetate.
7. A process as claimed in any one of the preceding claims wherein the ester comprises an ethyl ester.
8. A process as claimed in any one of the preceding claims wherein the ester comprises ethyl acetate.

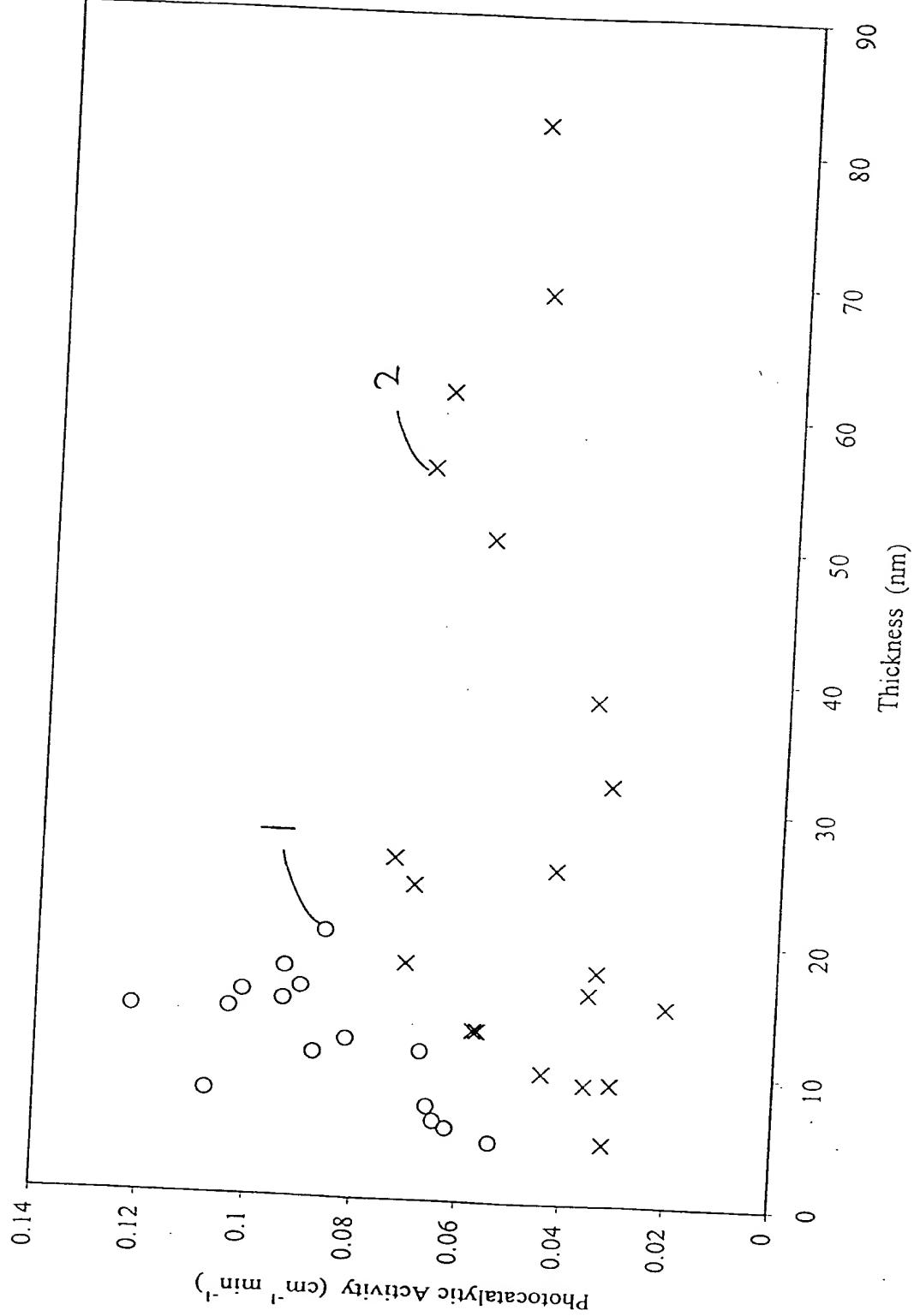
9. A process as claimed in any one of the preceding claims wherein the ester is the only source of oxygen in the fluid mixture.
10. A process as claimed in any one of the preceding claims wherein the surface of the substrate is contacted with the fluid mixture when the substrate is at a temperature in the range 200°C to 750°C.
11. A process as claimed in any one of the preceding claims wherein the surface of the substrate is contacted with the fluid mixture when the substrate is at a temperature in the range 400°C to 750°C.
12. A process as claimed in any one of the preceding claims wherein the surface of the substrate is contacted with the fluid mixture when the substrate is at a temperature in the range 600°C to 750°C.
13. A process as claimed in any one of the preceding claims wherein the fluid mixture comprises a gaseous mixture.
14. A process as claimed in any one of the preceding claims wherein the substrate comprises a glass substrate.
15. A process as claimed in any one of the preceding claims additionally comprising depositing an alkali metal ion blocking layer on the surface of the substrate before depositing the titanium oxide coating.
16. A process as claimed in any one of the preceding claims wherein the process is performed on-line during the float glass production process and the substrate comprises a glass ribbon.

17. A process as claimed in claim 16 wherein the process is performed in the float bath.
18. A process as claimed in any one of the preceding claims wherein the process is performed at substantially atmospheric pressure.
19. A process as claimed in any one of the preceding claims wherein the titanium oxide coating has a thickness of less than 30 nm.
20. A process as claimed in any one of the preceding claims wherein the titanium oxide coating has a thickness of less than 20 nm.
21. A process as claimed in any one of the preceding claims wherein the titanium oxide coating has a thickness in the range 2 nm to 20 nm.
22. A coated substrate produced by a process according to any one of the preceding claims.
23. A coated glass produced by a process according to any one of claims 14-21.
24. A coated glass comprising a glass substrate having a photocatalytically active titanium oxide coating on one surface thereof, characterised in that the coated surface of the glass has a photocatalytic activity of greater than $8 \times 10^{-2} \text{ cm}^{-1} \text{ min}^{-1}$ and in that the coated glass has a visible light reflection measured on the coated side of less than 20%.
25. A multiple glazing unit comprising a first glazing pane of a coated substrate produced by a process according to any one of claims 1- 22 in spaced opposed relationship to a second glazing pane.

26. Laminated glass comprising a first glass ply of a coated glass produced by a process according to any one of claims 14-21, a polymer interlayer, and a second glass ply.
27. A process for the production of a photocatalytically active coated substrate substantially as described hereinbefore with particular reference to any of the Examples.

AbstractImproved Process for Coating Glass

A process for the production of a photocatalytically active coated substrate comprising depositing a relatively thin titanium oxide coating on the surface of the substrate using a mixture of titanium chloride and an ester. The coating has a thickness of less than 40 nm. The coated substrate has a surprisingly high photocatalytic activity and low visible light reflection. Preferably the ester is an alkyl ester having an alkyl group with a β hydrogen, most preferably the ester is ethyl acetate. The preferred substrate is glass.



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